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Morphological Structure Characteristic And Quality of Semi Refined Carrageenan Processed By Different Drying Methods

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Abstract

Heat penetration during drying process of seaweed will rupture the seaweed cell wall. Different drying methods (drying with an oven, sun drying and solar tunnel drying) to produce Semi refined carrageenan (SRC) from *Kappaphycus alvarezii* have been studied. The aims of the study was to compare physicochemical characteristic of SRC on follow the morphological and functional group structure images and the quality of the product. The results indicated that different drying methods in the production of SRC made of *Kappaphycus alvarezii* did not give any difference to the morphological structure among the products. All samples showed an amorphous shape. The bands of the SRC product was at 2924,09 cm^{-1},1558 cm^{-1}, 1072,42 cm^{-1} respectively which indicated that products contained aliphatic, carboxyl, and glycosidic linkage. Spectra at absorption band of 848,68 cm^{-1} is related to sulphation level of *K. alvarezii* which is kappa-carrageenan origin. The finest structure of SRC was resulted from solar tunnel drier which result in high gel strength and lowest sulphate content.

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Keywords: *Kappaphycus alvarezii*; Drying methods; SCR; SEM; FTIR

1. Introduction

Cultured seaweed is dominated by red algae containing carrageenan which is important for industrial uses. Recently *Kappaphycus alvarezil* which is one of red algae species develop sharply in Indonesia. Traditionally seaweeds are processed by sun drying method which is dried in open air either using racks or they just lied on the surface area. During harvesting time the production is usually abundant which requires a large open area for drying, consequently it gives a problem if the area is limited. Solar drying method and mechanical

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drying method such as drying with an oven could be an alternative way in order to overcome such problems, in addition contamination from the open air could be reduced. However, there is very limited data available on the quality of SRC made from *Kappaphycus alvarezii* processed by different drying methods.

The cell wall of algae is composed by at least two different layers. The outer cell wall is an amorphous embedding matrix with cellulose fibers and phospholipid contents. While the inner cell wall contains fibrillar skeleton, alginate and fucoidan matrix, both imparts rigidity to the cell wall. The red algae cell wall is mainly comprised of sulphated polysaccharides (1). During drying process of seaweed samples, possible losses could be attributed to stress the plant due to loss of water and rupture cell walls since there is heat penetration to the cell wall. *K. alvarezii* contains a large amount of polysacharides (galactans) which could be broken down during extraction.

The aims of the study were to compare physicochemical characteristic of SRC and followed by analyzing the morphological and functional group structure images and the quality of the product

Materials and Methods

Samples Preparation

Semi Refined Carrageenan (SRC) was produced by processing the thallus of *K.alvarezii* (red algae) samples harvested after 45 days cultured in Karimun Jawa coastal water of Central Java. After removing excess soil and salt on the surface of thallus with running water, the seaweed were boiled at 80°C in an aqueous solution of 6% KOH for 4 hours. The thallus samples were neutralized with running water and dried. Each of samples was treated randomly to 3 different drying method treatments as follow : one of the sample was dried with an mechanical oven at temperature range of 40-50°C for 4 hours. The other sample was dried by sun drying methods for 8 hours and another sample was dried with a solar tunnel drier at temperature range of 30-40°C and the relative humidity (RH) of 80 % for 12 hours. After drying process, each sample was ground with a miller 0.6 mm in mesh size.

Scanning Electron Microscopy (SEM)

The surface morphology and pore size of the SRC samples were tested using Scanning Electron Microscopy (SEM JSM-6510LA, JEOL, Tokyo, Japan). Briefly, SRC samples were fixed on carbon tape, then dried under vacuum and platinum coated before examining (3).

Fourier Transform Infrared (FTIR) Spectroscopy

Two milligrams of the SRC sample were mixed with 200 mg KBr (FTIR grade) and pressed into a homogenous pellet. The pellet was immediately put into the sample holder FTIR Spectrophotometer Prestige-21 and spectra bands were recorded in the range of 4000-400cm^{-1} (2).

Measurement of gel Strength of SRCs, Viscosity, Sulphate Content and Colour measurement.

Gel strength of the samples were measured by preparing a hot SRC solution (1,6 % of SCR powder was diluted into a hot aqueous KCl solution). It was then kept in a refrigerator temperature for overnight. The gel strength of the sample was measured using TA-XT Plus Texture Analyser. The instrumental texture profile in a texture analyser. A commercial export quality SRC product produced by one of enterprises in Indonesia was used as a quality comparison. The viscosity was measured with a Brookfield DV-E viscometer at temperature of 25°C (3 g of SRC sample was diluted into 250 ml aquadest). Sulphate content was determined by a sulphate hydrolysis followed by precipitation of sulphate as barium sulphate. Colour of SRC products was measured by Hunterlab Colorimeter.

Statistical Analysis

Scanning Electron Microscopy (SEM) images and FTIR bands describing of SRC samples and commercial SRC were compared to references. Data of gel strength, viscosity and sulphate content are subjected to Analysis of Variance (Anova). Mean comparison was carried out using Tukey's Multiple range test.

Results and Discussions

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) images (magnification of 100x) base on different drying method are shown in Fig.1 (A, B, C,and D). The results of SEM showed that different drying methods in the production of SRC did not give any difference to the morphological shape of SRC samples but their diameter size differ from the commercial SRC. The images showed an amorphous, irregular shape and uniform distribution.

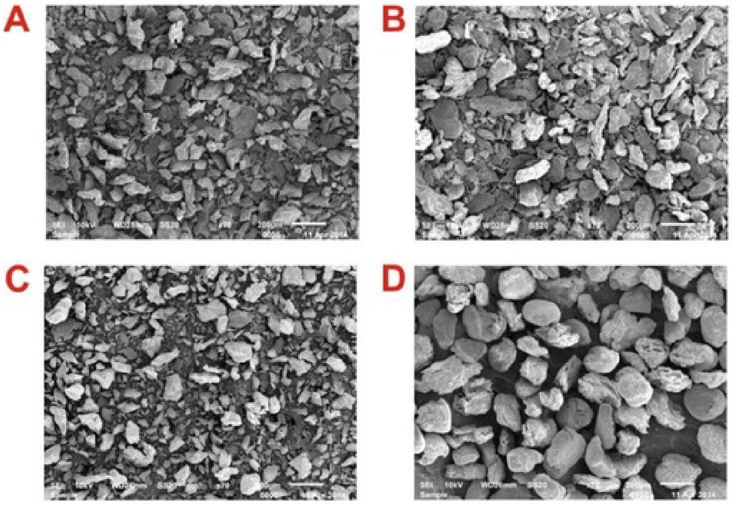


Fig. 1. SEM of Semi Refined Carrageenan powder (magnification of 100x): (A) Sun Drying , (B) Solar Tunnel Drying , (C) Oven and (D) Commercial

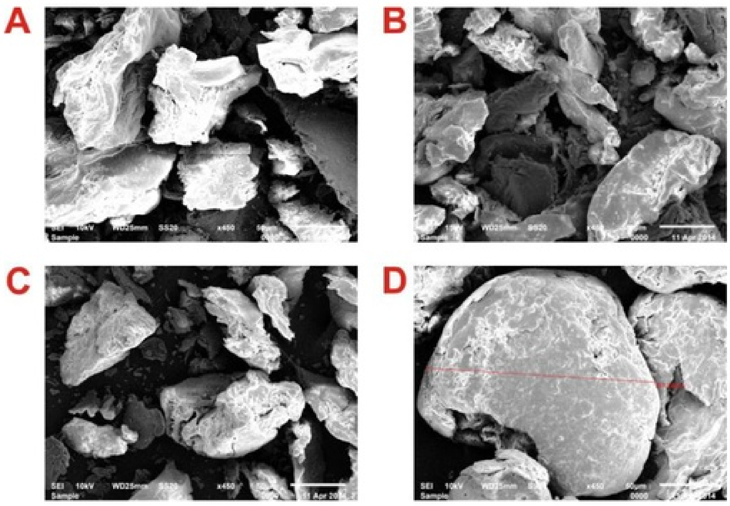


Fig 2 : SEM of Semi Refined Carrageenan powder (magnification of 450x): (A) Sun Drying , (B) Solar Tunnel Drying , (C) Oven and (D) Commercial

It can be seen from Fig. 2, (magnifications of 450x), commercial images sample has a diameter of 207.19 µm while the microstructure diameter of the samples were less than 200Å and their shape were irregular which were smaller compared to that of commercial SRC.

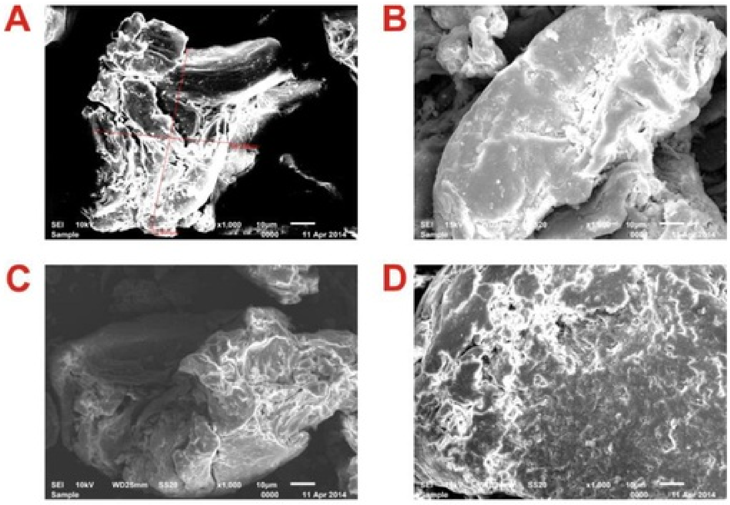


Fig. 3. SEM of Semi Refined Carrageenan powder (magnification of 1000x): (A) Sun Drying , (B) Solar Tunnel Drying , (C) Oven and (D) Commercial.

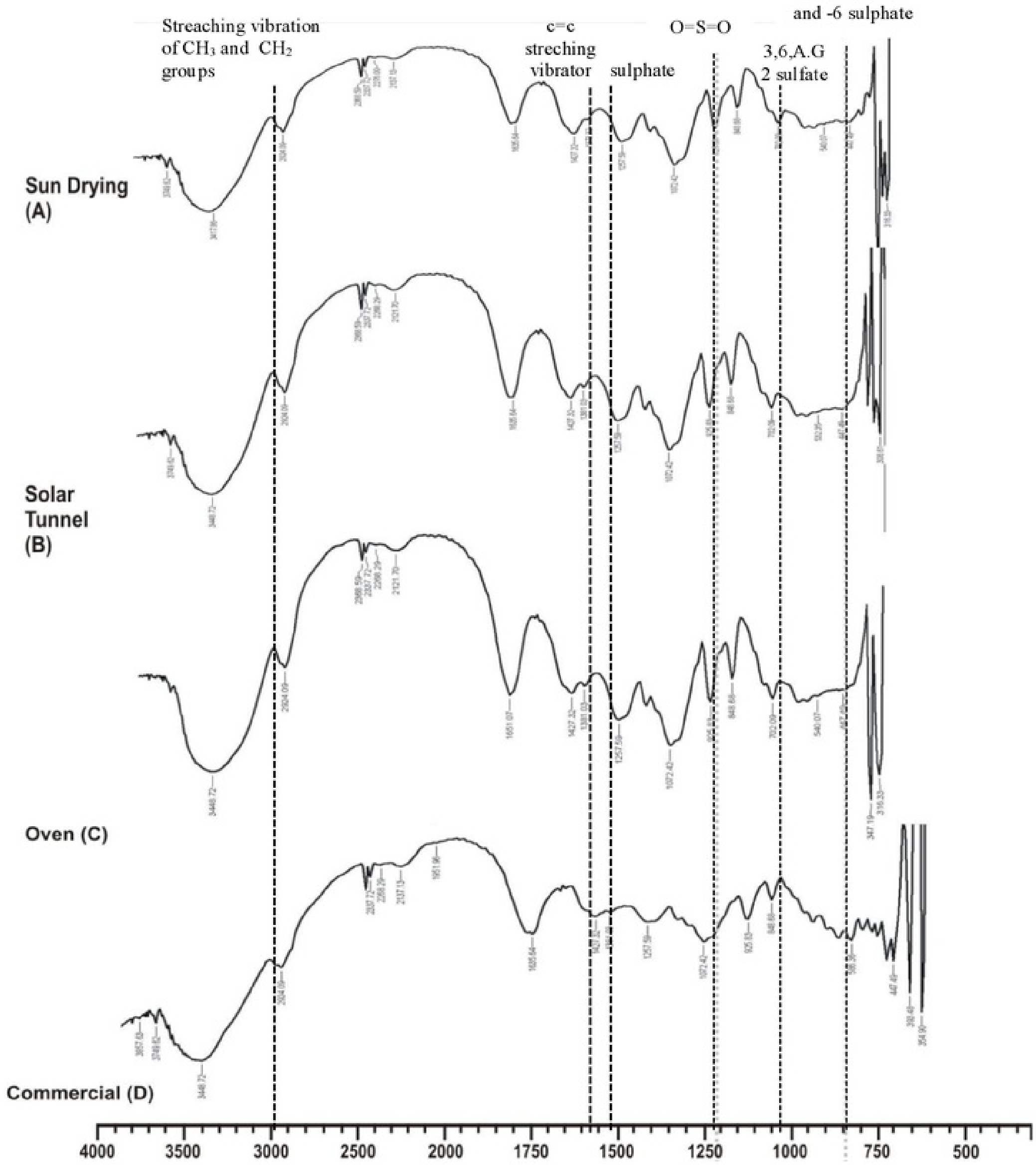
Based on Fig. 3 (magnification of 450x) it was observed that sample SRC produced by sun drying process is predominantly rough heterogenic surfaces distributed with an average size of 56-75 µm. The commercial sample has granular form and well distributed than others samples. The texture of SRC depends on the ways they were processed. Therefore, the different characteristics observed in the results were due to the drying methods. It was similar to the result of fresh seaweed thallus samples have rounded or granular cell wall (3). During drying heat would penetrated through cell wall membranes and it would disruption to changes the structure. In the studies of ultrastructure of cellulose microfibrils by electron microscope, it is shown that the structure is usually flattened with diameter on the range between 100-200Å. Furthermore another study reported that during drying process fresh apple tissue has a well-organized structure consisting of cells and intercellular spaces, however, the breakdown of cell walls, a decreased intercellular contact and collapse of cell structure (4).

SRC Identification

FTIR identification for SRC powder on the different methods of drying, in the range 4000 - 400 cm^{-1} are presented in Fig 4. In general, all drying process methods did not result in changed on pattern of the bands appeared on the samples. The band on 2924 cm^{-1} and 2854 cm^{-1} were both appread on a weak bands. It were probably due the stretching vibration. Not only for the same band found on the same red algae such as *G. corticata* but the stretching vibration also found in the brown algae (5). The same weak band due to the stretching vibration of CH3 and CH2 (5) research. The weak band around 1558 cm^{-1} was represented C=C stretching vibration indicated of lignin components (6). An absorption band occurs around 1457 cm^{-1} in all samples showed the presence of C-O stretching and O-H bending vibration (carboxylic acid). The characteristic broad band of sulphate esters (S=O) was observed between 1210-1260 cm^{-1} for all samples (7- 9).

The band at 1072,42 cm^{-1} indicated aliphatic, carboxyl and glycosidic linkage similar to that reported by (5). Furthermore a band at 1531 cm^{-1} was commonly found for all algae species (10). The bands at about 1235cm^{-1} represented $-SO_3$ stretching were mainly present in sulfonic acids of polysaccharides, such as fucoidan. The band at 1022 cm^{-1} was assigned to the C-O stretching of alcohol groups. All samples also showed characteristic spectra at absorption band at 848,68 cm^{-1} that corresponded to sulphation (galactose-4-sulphate level) of

K. alvarezii which was kappa- carrageenan origin (11- 12). Those all finding were agreed to the previous study done at different coastal water area in Indonesia (13) and it may corresponded to the S=O (2). The FTIR pattern was presented similar values to that for commercial sample.



Wave number (cm-1)

Fig 4. FTIR Analysis of Semi Refined Carrageenan powder
(A) Sun Drying , (B) Solar Tunnel Drying , (C) Oven and D) Commercial

Gel strength, viscosity, sulphate content and colour measurements

Data on gel strength, viscosity, sulphate content and colour measurement are presented on Table 1.

Table 1. Gel strength, viscosity, sulphate content and colour measurement of SRC products

Parameters	Sample		
	Sun drying	Solar tunnel drying	Oven drying
Gel strength (gf)	776,53 ± 37,15[b]	920, 49 ± 31,56[a]	694, 44 ± 40,71[c]
Viscocity (cp)	16,17 ± 0,17[a]	15,55 ± 0,34[b]	16,37 ±0,16[a]
Sulphate (%)	15,12 ± 0,21[a]	13,12 ± 0,03[c]	13,37 ± 0,26[b]
Colour	76,90[a]	74,97 [b]	70,19[c]

Gel strength, a parameter of great value commercially, presented different values for different samples. The gel forming process is highly sensitive to structural and compositional characteristic of SRC (14- 18). The highest gel strength was obtained from SRC produced by solar tunnel dyring,followed by sun drying which were follow : 920, 492 gf ± 31,56 , 776,535 gf ± 37,15 and 694, 449 gf ± 40,71 and there were a significant different among samples. The gel strength presents a negative correlation with sulphate content, the highest the gel strength the lowest the sulphate content . The viscosities sample showed a significant different between solar tunnel drying with both sun drying and oven drying samples. SRC resulted form oven drying achieved the highest value of darkness while the lowest values was commercial.

Conclusion

The results of SEM showed that different drying methods in the production of SRC did not give any difference to the morphological shape among the products. The changes in shape and volume of samples was observed for all the drying methods studied, but it did not give any differences on the FTIR pattern of SRC products. The finest structure of SRC was resulted from solar tunnel drier which result in high gel strength and lowest sulphate content.

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